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(54) **Biocidal composition**

(57) A method of controlling biological growth and corrosion in an aqueous system, preferably an industrial aqueous system such as an industrial cooling water system, which comprises treating said system with hydrogen peroxide or a source thereof.

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BIOCIDAL COMPOSITION

The present invention relates to the treatment of aqueous systems, especially industrial water systems such as industrial water cooling systems, for example evaporative, open circulating systems and condensing systems (eg dehumidifiers and air-conditioning).

The largest industrial use of water is as a coolant. The water used for this purpose is typically derived from natural sources such as seawater, lakes and rivers and is, of course, not sterile. Microorganisms, for example bacteria and fungi are able to proliferate in this water and can cause problems by their accumulation. For example, it is well-known that the accumulation of bacteria in water systems commonly gives rise to slimy deposits on the surfaces of the system which contact the water. The build-up of such deposits in cooling water systems can reduce heat transfer between heat exchange surfaces, inhibit water flow and foul the components of the water system thereby increasing energy costs, reducing output or both.

A further problem encountered in such aqueous systems is that the water used tends to contain components such as sulphate and chloride ions which attack the materials from which the apparatus of the system is constructed, usually iron and iron-based alloys such as mild steel. This problem is more pronounced when the concentration of aggressive components increases, for example when a portion of water in the aqueous system is evaporated, and in

systems where water is recirculated such as in cooling water systems. The corrosive action of the water can cause premature equipment deterioration or failure which can lead to unscheduled shutdowns.

These problems may be controlled by use of a variety of additives which control separately biological growth and corrosion in the aqueous system. The additives must be chosen carefully to avoid any adverse interaction between the biocidal and corrosion inhibiting components.

The most common method of controlling biological, for example bacterial, growth in aqueous systems is by the use of biocides. Biocides may be oxidizing or non-oxidizing. By far the most commonly used oxidizing biocide is chlorine which may be added to the water as a gas or in the form of a chlorine-yielding compound, for example sodium dichloroisocyanurate. However, oxidizing biocides such as chlorine tend to corrode the materials from which aqueous systems are typically made and are, furthermore, toxic and therefore unacceptable from an environmental view point. These disadvantages have restricted the use of biocides such as chlorine and its compounds. Inorganic biocides such as compounds of mercury and arsenic may also give rise to environmental pollution. Quaternary ammonium compounds have been widely used as non-oxidizing biocides. None of the biocides described above is known to control corrosion in aqueous systems.

Corrosion in aqueous systems is typically controlled by the use of chemical corrosion inhibitors. For example,

in the past chromates and inorganic polyphosphates have been used. While the chromates are highly effective at controlling corrosion, they are highly toxic and consequently present handling and disposal problems. The polyphosphates are relatively non-toxic, but tend to hydrolyze forming orthophosphates. Orthophosphates themselves can result in the formation of scale and cause sludge problems in the system.

To the applicants' knowledge no single reagent is available which can provide adequate control of biological growth and corrosion in aqueous systems.

With this background in mind, the present invention seeks to provide a method of controlling or inhibiting biological growth and corrosion in aqueous systems which is non-polluting, and therefore environmentally friendly, and which uses a single active species therefore overcoming the problem of matching biocidal and corrosion inhibiting components.

The antimicrobial activity of hydrogen peroxide is well-known. Indeed, there are several commercially available formulations containing  $H_2O_2$  for use as a disinfectant. In such disinfectant formulations the  $H_2O_2$  is usually present in an amount of at least 30% by weight. However, even dilute solutions of  $H_2O_2$  are known to cause unacceptable levels of corrosion in many materials, for example carbon steel (Corrosion Resistance Tables, Philip A. Schweitzer, Marcel Dekker Inc).

However, it has now been found that it is possible to

use  $H_2O_2$  as a biocide in an aqueous system without the associated problems of it corroding the materials which it contacts. Surprisingly, it has been found that when used at low concentration  $H_2O_2$  actually has a corrosion inhibiting effect. As  $H_2O_2$  yields only water and oxygen on decomposition it does not cause environmental problems such as those experienced with prior biocides such as chlorine.

Accordingly, the present invention provides a method of controlling biological growth and corrosion in an aqueous system which comprises adding to the system hydrogen peroxide or a source thereof, monitoring the rate of corrosion of a metal surface in the system and, if the rate is unacceptable, adding more hydrogen peroxide. The use of hydrogen peroxide is preferred.

The method of the invention may be employed in any aqueous system where it is desired to control or inhibit biological growth and corrosion. The aqueous system is preferably an industrial aqueous system, in particular an evaporative, open recirculating system such as an industrial cooling water system.

Such a cooling system is typically constructed of iron or an iron-based alloy, for example mild steel. Evaporators, single and multi-pass heat exchangers and cooling towers are examples of elements of a cooling system constructed of such materials where the control or inhibition of biological growth and corrosion is typically required.

By the term biological growth is meant for example

bacteria which may be aerobic, eg *Pseudomonas* species, *Klebsiella* species, *Enterobacter* species, *Flavobacterium* species, *Bacillus* species and *Gallionella* species, or anaerobic, eg *Desulfovibrio* species and *Desulfotomaculum* species, algae such as *Chlorella vulgaris*, *Diatomeae* (eg *Navicula pelliculora*), *Anabaena oscillarioides* and *Oscillatoria rubescens*, and fungi such as those belonging to the genera *Ascomycetes*, *Basidiomycetes* and *Fungi Imperfecti*, eg *Poria* species and *Stemphylium* species, commonly found in the water used in industrial aqueous systems.

The aqueous systems in which the method of the invention may be employed are generally saturated with dissolved oxygen, and have a pH of from 6 to 10 and a conductivity (arising from, eg dissolved salts) of from 400 to 3000  $\mu\text{S}/\text{cm}$ . The pH and oxygen content of the water are not generally critical.

The method of the invention requires the use of  $\text{H}_2\text{O}_2$  or a compound which yields  $\text{H}_2\text{O}_2$  on addition to the aqueous system.  $\text{H}_2\text{O}_2$  reacts with, for example borates, pyrophosphates, sulphates, and certain organic carboxylic acids to give usually stable solid peroxygen or peroxyhydrate compounds. These compounds hydrolyze readily in solution to give  $\text{H}_2\text{O}_2$ , and are therefore convenient solid sources of  $\text{H}_2\text{O}_2$ . Sodium perborate is perhaps the most commonly used solid source of  $\text{H}_2\text{O}_2$ , being available in the tetrahydrate form,  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ . The tetrahydrate may be formed by treating a borax solution with  $\text{H}_2\text{O}_2$  and sodium

hydroxide.

To be effective in the method of the invention, the hydrogen peroxide should generally be present at a concentration of from 25 to 100 ppm, preferably of from 40 to 80 ppm, and, in particular at a concentration of about 50 ppm. These concentrations are expressed as the concentration of active  $H_2O_2$ . If a source of  $H_2O_2$  is used it should be added in an amount which will give the required  $H_2O_2$  concentration when it is hydrolyzed.

The concentration of hydrogen peroxide which is required in the method of the invention typically depends upon the degree of corrosion inhibition required, the presence of substances which cause decomposition of hydrogen peroxide, for example metal ions and metal oxides, and the amount of biological material present.

The method of the invention is generally employed for water temperatures in the range of from 20 to 80°C, preferably from 40 to 60°C, and, in particular at a temperature of about 45°C.

In a cooling water system it is useful to introduce the  $H_2O_2$  or source thereof into the system at any location where it will be quickly and efficiently mixed with the water, although it will generally be most convenient to add it to the system via the make-up or feed water lines through which water enters the system. The hydrogen peroxide concentration in the water may be monitored and adjusted from time to time to maintain the desired  $H_2O_2$  concentration.

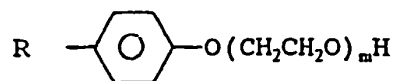
The hydrogen peroxide may be provided to the aqueous system in liquid or solid form. As a liquid it is preferred to add the hydrogen peroxide as a solution containing from 5 to 30% by weight of  $H_2O_2$ , more preferably still from 15 to 25% by weight and, particularly, about 20% by weight. The solution is added in an amount which will give the appropriate  $H_2O_2$  concentration in the aqueous system. It is, of course, possible to use concentrated solutions of  $H_2O_2$  for dilution before or on addition to the aqueous system.

As a solid the hydrogen peroxide may be provided as a compound readily hydrolyzable to  $H_2O_2$  as described above.

Preferably, the composition of the invention is a liquid. It is expected that when the composition is provided in liquid form the solvent will be water.

The present invention also provides a composition suitable for treating industrial aqueous systems which comprises hydrogen peroxide or a source thereof and an industrial water treatment additive, for example a dispersant.

Examples of suitable dispersants include cationic, anionic, non-ionic or amphoteric surfactants. Typical surfactants which may be used include ethylene oxide adducts, especially ethoxylated phenols of general formula:



wherein  $m$  represents 2 to 40 and  $R$  represents  $C_nH_{2n+1}$  in



which n is from 0 to 18, as well as alkylamine polyoxypropylene-polyoxyethylene adducts and alkylolamides.

Preferred ethoxylates are those derived from phenol itself, nonyl phenol and dodecyl phenol and those containing 4 to 15 ethoxylate groupings.

Typical alkylamine polyoxypropylene polyoxyethylene adducts include N,N,N'-polyoxyethylene-polyoxypropylene-ethylenediamine block copolymers such as those of formula:



in which each x and y has a value which can differ from one block to the next. These materials are available as "Tetronics".

Typical alkylolamides which can be used include those derived from fatty acids containing for example 8 to 18 carbon atoms, such as coconut oil fatty acids, and an alkanolamine, preferably ethanolamine or diethanolamine. Some such materials are commercially available under the Concenstate trade marks.

Alternatively, the dispersant may be a polymeric or copolymeric dispersant, for example poly(acrylic acid) and its salts, acrylamide-acrylic acid copolymers, poly (maleic acid) or sulfonated polymers.

Typically the dispersant/surfactant to hydrogen peroxide ratio is about 5:200.

The compositions of the invention may also comprise other water treatment additives such as scale and corrosion inhibitors. As scale and corrosion inhibitors, any formulations may be used which are compatible with the

hydrogen peroxide. For example, the composition may comprise Polymate 5637, a corrosion and scale inhibiting formulation commercially available from Grace Dearborn. It has been found that formulation with Polymate 5637 gives a significant reduction in the corrosion rate observed.

The compositions of the invention generally comprise from 5 to 30% by weight of hydrogen peroxide or equivalent when a hydrogen peroxide source is used. According to a preferred embodiment, the composition comprises from 15 to 25% by weight  $H_2O_2$  or equivalent  $H_2O_2$  source. Particularly preferred is a composition comprising about 20% by weight  $H_2O_2$  or equivalent  $H_2O_2$  source.

The present invention will now be illustrated with reference to the following Example.

#### EXAMPLE 1

Experiments were carried out to measure the corrosion rate of mild steel in aqueous media. Coupons of mild steel were submerged in test solutions at 45°C. The composition of the test solutions is given in the Table below.

In those experiments requiring  $H_2O_2$  it is added daily to maintain a concentration of 50 ppm.

In those experiments requiring Polymate 5637 it is added in a single addition to give a concentration of 100 ppm.

After seven days the coupons were removed from solution and analysed. The corrosion rates given in mils per year (mpy) are as shown in the Table below.

<u>Experiment</u>	<u>Composition of test medium</u>	<u>Corrosion Rate (mpy)</u>
1	T.W.1	4.21
2	T.W.1 + 50 ppm H <sub>2</sub> O <sub>2</sub>	1.19
3	T.W.2 + 100 ppm Polymate 5637	12.7
4	T.W.2 + 50 ppm H <sub>2</sub> O <sub>2</sub> + 100 ppm Polymate 5637	0.09

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T.W.1 = Test water 1

T.W.2 = Test water 2

The corrosion rate is calculated from the change in weight of the coupon.

The characteristics of the test waters 1 and 2 are as follows:

	<u>Test Water 1</u>	<u>Test Water 2</u>
pH:	8.2	8.2
TAC:	120 ppm CaCO <sub>3</sub>	300 ppm CaCO <sub>3</sub>
TCa:	160 ppm CaCO <sub>3</sub>	500 ppm CaCO <sub>3</sub>
Cl:	52 ppm	

TAC stands for m-alkalinity expressed as ppm CaCO<sub>3</sub>;

p-alkalinity is zero at the pH of the experiments.

TCa stands for the calcium hardness of the water expressed in ppm CaCO<sub>3</sub>.

Cl represents the chloride ion concentration.

CLAIMS

1. A method of controlling biological growth and corrosion in an aqueous system which comprises adding to the system hydrogen peroxide or a source thereof, monitoring the rate of corrosion of a metal surface and, if the rate is unacceptable, adding more hydrogen peroxide.
2. A method according to claim 1, wherein the aqueous system is an industrial aqueous system.
3. A method according to claim 2, wherein the aqueous system is an industrial cooling water system.
4. A method according to any one of the preceding claims wherein the hydrogen peroxide concentration is from 25 to 100 ppm.
5. A method according to according to claim 4, wherein the hydrogen peroxide concentration is from 40 to 80 ppm.
6. A method according to any one of the preceding claims, wherein the temperature is from 20 to 80°C.
7. A method according to claim 6, wherein the temperature is from 40 to 60°C.
8. A method according to claim 1 substantially as hereinbefore described.
9. A composition suitable for use in the method claimed in any one of claims 1 to 8, which comprises hydrogen peroxide or a source thereof and an industrial water treatment additive.
10. A composition according to claim 9 comprising from 5 to 30% by weight of hydrogen peroxide or equivalent

when a hydrogen peroxide source is used.

11. A composition according to claim 10 comprising from 15 to 25% by weight of hydrogen peroxide or equivalent when a hydrogen peroxide source is used.

12. A composition according to any one of claims 9 to 11 wherein the industrial water treatment additive is a dispersant.

13. A composition according to claim 9, substantially as hereinbefore described.

14. A product, comprising hydrogen peroxide and an industrial water treatment additive, for simultaneous, separate or sequential use in controlling biological growth and corrosion in an aqueous system.

**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

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**Relevant Technical Fields**

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R I W Honeywood

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26 September 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASE - WPI

Documents considered relevant  
following a search in respect of  
Claims :-  
1-14

**Categories of documents**

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| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step 11 combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
|--|---|

Category	Identity of document and relevant passages	Relevant to claim(s)
X	WO 91/15122 A1 (MINNTECH CORPORATION)	1,9 and 14 at least
X	US 4806169 (SPANNE)	1,9 and 14 at least
X	WPI Accession number 92-044877/06 and JP 3288585 TAIHO KOGYO KK - see abstract	1,9 and 14 at least
X	WPI Accession number 79-53706B/29 and JP 54073119 CLEAN LIFE KOGYO KK - see abstract	1,9 and 14 at least

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